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A METAL-CENTERED RADICAL-PAIR MECHANISM FOR ALKYNE  
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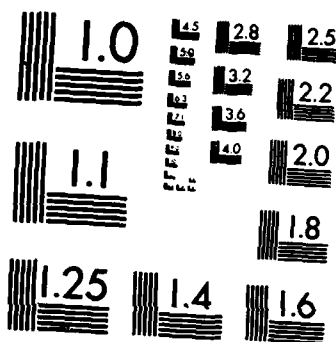
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A Metal-Centered Radical-Pair Mechanism for Alkyne Hydrogenation With  
A Binuclear Rhodium Hydride Complex. CIDNP Without Organic Radicals

by

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A BINUCLEAR RHODIUM HYDRIDE COMPLEX. CIDNP WITHOUT ORGANIC RADICALS

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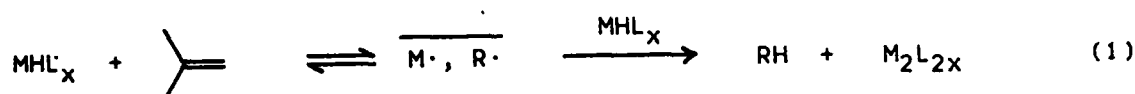
**Abstract:** The binuclear complex  $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dppm})_2$ , 1, reacts with alkynes under  $\text{H}_2$  to form the corresponding olefins with predominantly cis addition, and an alkyne-bridged A-frame complex. Specific alkynes studied include  $\text{PhC}\equiv\text{CH}$ ,  $\text{MeC}\equiv\text{CH}$ ,  $t\text{-BuC}\equiv\text{CH}$ ,  $\text{EtOC}\equiv\text{CH}$ ,  $\text{HC}\equiv\text{CCOOMe}$ ,  $\text{HC}\equiv\text{CCH}_2\text{OH}$ , and  $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{OH}$ . In all of the hydrogenation reactions, CIDNP is observed with major polarizations occurring as multiplet effects in the trans and geminal proton resonances of the product olefins. Specific labelling studies using  $1 + \text{PhC}\equiv^{13}\text{CH}$ ,  $\text{Ph}^{13}\text{C}\equiv\text{CH}$ , and  $\text{PhC}\equiv\text{CD}$ , and  $1\text{-d}_2 + \text{PhC}\equiv\text{CH}$  show no polarization due to  $^{13}\text{C}$  hyperfine coupling, and major polarizations only in those protons originally on the binuclear complex 1. These studies, together with radical trapping experiments, lead to the conclusion that the radical pair responsible for the observed CIDNP is metal-based and does not involve alkenyl radicals. The basis of the observed CIDNP thus differs from the previously described mechanism of H-atom transfer between a transition metal hydride and an organic substrate. The present results are consistent with a new mechanism in which a metal-centered biradical acts as the radical pair leading to the observed polarization effects.



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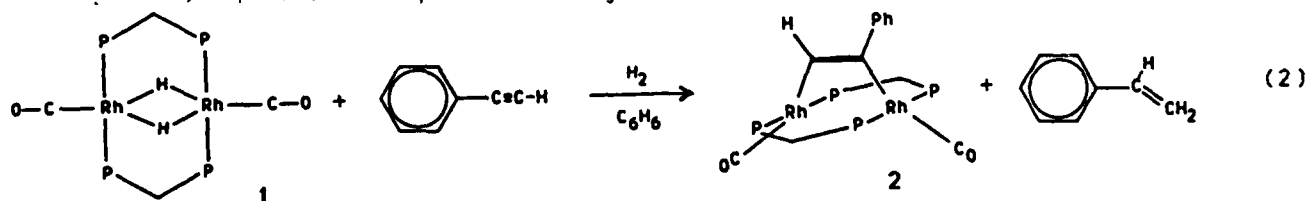
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A radical pair mechanism for the hydrogenation of unsaturated substrates by mononuclear transition metal hydrides has been demonstrated by the occurrence of chemically induced dynamic nuclear polarization or CIDNP.<sup>1-4</sup> In this mechanism, an  $\overline{M\cdot}, R\cdot$  radical pair forms by H atom transfer, eqn (1), and leads to the observed CIDNP through singlet-triplet mixing and spin selective reactions. The reactant and product resonances in these reactions show net polarization which is explained by the difference in g values of the radical pair components,  $M\cdot$  and  $R\cdot$ .<sup>1</sup> In this communication, we report that CIDNP also



occurs in the hydrogenation of alkynes by  $Rh_2H_2(CO)_2(dppm)_2$ , 1,<sup>5</sup> but that the basis for CIDNP in this system is different, involving an extraordinary metal-centered biradical.<sup>6</sup>

Complex 1 reacts rapidly with  $PhC\equiv CH$  in  $C_6D_6$  under  $H_2$  to give ~1 equivalent of styrene and an intense blue complex, 2, which shows NMR resonances characteristic of an unsymmetrical alkyne-bridged A-frame structure, eqn (2).<sup>7</sup> Complex 2 slowly converts to the more stable isomer



containing a  $\mu_2, \eta^2$ -alkyne bridge which has been reported previously along with the isomeric vinylidene complex,  $Rh_2(\mu-C=CHPh)(CO)_2(dppm)_2$ .<sup>8</sup> The addition of hydrogen to  $PhC\equiv CH$  in (2) is predominantly cis as evidenced by relative amounts of isotopomers formed when using either 1 +  $PhC\equiv CD$  under  $H_2$ , or  $Rh_2D_2(CO)_2(dppm)_2$ , 1- $d_2$ , +  $PhC\equiv CH$  under  $D_2$ . Reaction similar to (2) occurs with a variety of alkynes including  $MeC\equiv CH$ ,  $t-BuC\equiv CH$ ,  $EtOC\equiv CH$ ,  $HC\equiv CCOOMe$ ,  $HC\equiv CCH_2OH$ , and  $CH_3C\equiv CCH_2OH$  leading in each case to formation of the corresponding olefin and

an intensely colored complex analogous to 2.

In all of these reactions, CIDNP is seen as shown in Figure 1 for eqn (2). The most striking aspects of the observed CIDNP of Fig. 1 are the strong absorption/emission (A/E) multiplet effect of the trans proton ( $\delta$  5.06;  $J_{HH} = 11$ , 1 Hz) of the product styrene, the unusual A/E/A/E multiplet effect of the geminal proton ( $\delta$  6.57; 18, 11 Hz), a weak and variable multiplet effect in the cis proton resonance ( $\delta$  5.59; 18, 1 Hz), and the absence of a net effect. Also seen is the resonance for dissolved  $H_2$  ( $\delta$  4.42) which shows an initial intensity three times greater than its long-term value. The reaction between  $EtOC\equiv CH$  and 1 produces completely analogous CIDNP results with little polarization of the cis proton resonance of the product olefin. In the reaction of 1 with other alkynes, the cis proton resonance shows different degrees of polarization, while the trans and geminal protons exhibit strong multiplet effects similar to those of Figure 1. These results indicate that a radical pair mechanism is followed in the hydrogenation of alkyne by 1, and  $\Delta g$  of the radical pair must be near zero to explain the absence of net effects in the observed CIDNP.<sup>9-12</sup> We can thus rule out a mechanism based on a  $M\cdot$ ,  $R\cdot$  radical pair similar to that invoked in previous studies using mononuclear transition metal hydrides.<sup>1-4</sup>

In order to probe the basis of CIDNP in eqn (2), a series of labelling experiments was performed, the results of which are shown in Figure 2. Trace 2a corresponds to the initial spectrum seen in Fig. 1. When either  $PhC\equiv^{13}CH$  or  $Ph^{13}C\equiv CH$  is used as the alkyne in (2), large coupling is seen between the  $^{13}C$  nucleus and the styrene proton(s) attached to it, but as shown in spectra 2b and 2c, no polarization occurs in the CIDNP due to  $^{13}C$  hyperfine. Spectrum 2b exhibits particular enhancement of the  $H_2$  absorption and a very slight net effect of the styrene trans and geminal resonances. In 2c the downfield half of the  $^{13}C$  coupled geminal resonance at  $\delta$  6.57 is obscured by aromatic proton resonances, while from 2d a value of 155 Hz is obtained for the  $^1J_{CH}$  coupling

using a mixture of  $\text{Ph}^{13}\text{C}\equiv\text{CH}$  and  $\text{PhC}\equiv\text{CH}$  in eqn (2). Spectrum 2c also shows a small resonance at  $\delta$  6.52 due to the  $\mu_2, \eta^2$ -alkyne bridged complex<sup>7</sup> which grows in slowly.

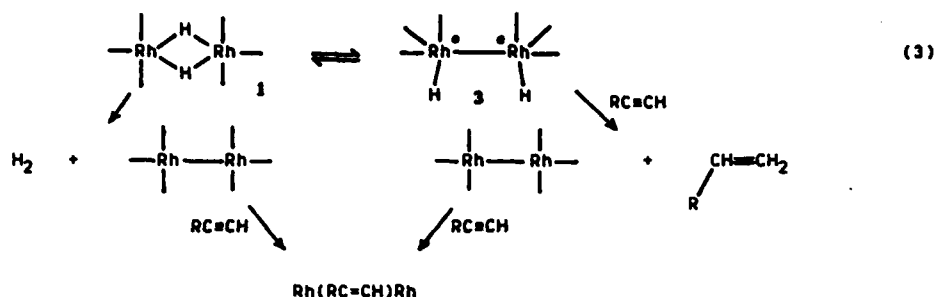
Deuterium labelling reveals a strong multiplet effect in the trans and geminal protons when  $\text{PhC}\equiv\text{CD}$  is reacted with 1 (spectrum 2e), and no CIDNP when  $\text{PhC}\equiv\text{CH}$  reacts with 1- $\text{d}_2$ . In the reaction leading to 2e, a small amount of  $\text{PhC}\equiv\text{CH}$  which is present accounts for the cis resonance at  $\delta$  5.59 and confirms an isotope shift of the trans resonance at  $\delta$  5.06. The major conclusions from these labelling studies are: (1) no polarization occurs for  $^1\text{H}$  and  $^{13}\text{C}$  nuclei which are part of the alkyne substrate throughout the course of the reaction, and (2) the only styrene protons showing polarization are those which originated on the binuclear complex  $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dppm})_2$ , 1.

Both the absence of polarization due to  $^{13}\text{C}$  hyperfine in spectra 2b-2d and the cis addition of hydrogen to  $\text{PhC}\equiv\text{CH}$  argue strongly against styrenyl radicals as components of the radical pair responsible for the CIDNP effect. This conclusion is further supported by the fact that efforts to block CIDNP by trapping styrenyl radicals using dihydroanthracene, 1,4-cyclohexadiene, and cumene have been unsuccessful. Moreover, when 1- $\text{d}_2$  and  $\text{PhC}\equiv\text{CD}$  are reacted in the presence of a 20-fold excess of cumene, no styrene containing olefinic protons is observed.

The results of our experiments lead us to the inescapable conclusion that the radical pair responsible for CIDNP in the reaction of 1 with alkynes must be a metal-centered biradical (MCBR). The major polarizations we see only occur in the hydrogens originally on 1. For a pure multiplet effect,  $\Delta g$  of the radical pair must be zero, but a radical pair based on styrenyl radicals is totally inconsistent with experiment. We therefore propose that 1 rapidly and reversibly forms a biradical isomer 3 which undergoes singlet-triplet mixing and spin-selective reaction to produce CIDNP. The "singlet" reaction channel of 3 is



recombination to 1, whereas the escape or "triplet" channel corresponds to reaction with  $\text{RC}\equiv\text{CH}$ , as shown in eqn (3).<sup>13</sup> Application of Kaptein's rule for



multiplet effects based on this analysis leads to the prediction of A/E polarization of the geminal and trans resonances in accord with our observations.<sup>14</sup> That the addition of  $\text{H}_2$  to the alkyne occurs with predominantly cis stereochemistry and very little or no net effect indicates that the biradical 3 transfers its H atoms to  $\text{RC}\equiv\text{CH}$  in an essentially concerted manner.

To our knowledge this is the first example of CIDNP based on a metal-centered biradical. Our CIDNP results may be compared with those of Closs and Kaptein for organic biradicals in which singlet-triplet mixing occurs by either a spin-sorting mechanism as is seen in the present study, or by  $T_1$ -S mixing which leads to emission effects exclusively.<sup>15</sup> The latter is dominant when the exchange integral  $J$ , which reflects the singlet-triplet splitting, is large and comparable to the Zeeman splitting; our results suggest that in the case of 3,  $J$  is relatively small. Further experimental and theoretical work on biradicals such as 3 is needed.

While the present study is the first to recognize the MCBR for producing CIDNP, one other report involving a polynuclear transition metal organo-metallic compound shows similar effects.<sup>16</sup> Specifically, Bergman, *et al.*, find multiplet effects in the hydrogenolysis of  $\text{Co}_3(\text{CO})_9(\mu_3\text{-CCH}_2\text{-t-Bu})$  to give  $\text{t-BuCHCH}_2$  with polarization only in the protons originating from  $\text{H}_2$ .<sup>16</sup> We think that that reaction may also proceed via a metal-centered biradical, and suggest that MCBR mechanisms which are difficult to detect may occur more commonly in

reactions involving polynuclear transition metal hydrides.

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7. Typically, 10 mg (0.01 mmoles) of **1** is dissolved in 0.5 ml  $C_6D_6$  under  $H_2$  in an NMR tube sealed with a septum. Addition of  $PhCCH$  (3  $\mu$ L, 0.03 mmoles) by syringe is followed immediately by placement in the probe of a Bruker WH-400 400 MHz NMR spectrometer. Spectroscopic data for **2**.  $^1H$  NMR ( $C_6D_6$ )  $-CH_2-$  region:  $\delta$  3.77 (m, 2 H), 2.64 (m, 2 H) with a geminal coupling  $^2J_{HH}$  of 12 Hz.  $^{31}P$   $\{^1H\}$  NMR:  $\delta$  23.0 (m) and 26.4 (m).  $^{13}C$   $\{^1H\}$

NMR for alkyne carbons: 150.1 (m, width ~70 Hz, PhCCH) and 174.1 (m, width ~70 Hz, PhCCH) with assignments made using specifically labelled PhCCH.

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13. Complex 1 undergoes facile loss of H<sub>2</sub> in the absence of other reagents.<sup>5</sup>  
This loss of H<sub>2</sub>, seen in the present study when reaction (2) is done under N<sub>2</sub> with lower resultant yields of styrene, is not necessary to explain the observed multiplet effects. However, in some experiments, significant enhancement of H<sub>2</sub> absorption is detected. This result cannot be explained by 3, and suggests the possibility of a second metal-centered biradical such as one with both H's on a single Rh center prior to H<sub>2</sub> reductive elimination. This observation is under continuing study.
14. The A/E phase of the multiplet effect is determined from Kaptein's rule<sup>11</sup> assuming a singlet precursor, escape or triplet products, a positive spin-spin coupling constant, and the fact that the coupled nuclei are on different radical centers of the MCBR.
15. (a) Closs, G. L.; Doubleday, C. E. J. Am. Chem. Soc. **1972**, 94, 9248.  
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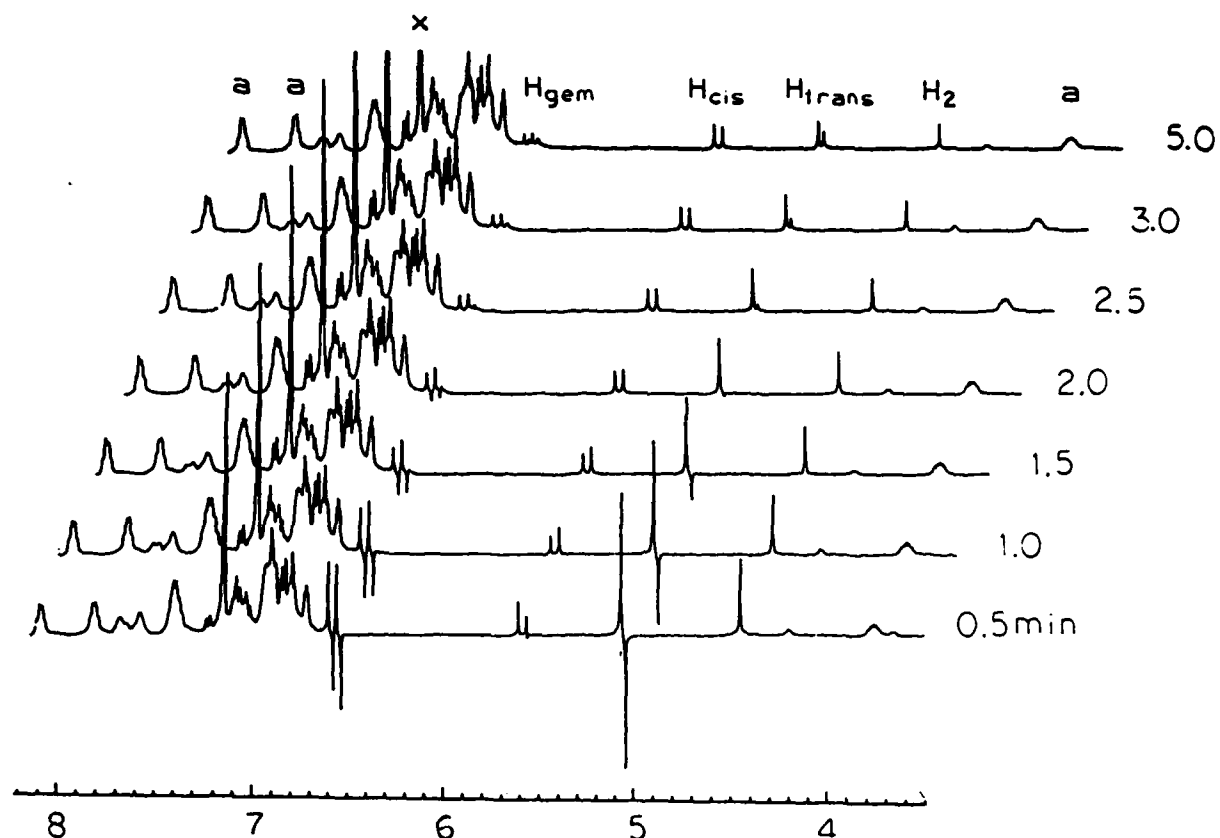


Figure 1.  $^1\text{H}$  NMR spectra at 400 MHz for the reaction of  $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dppm})_2$ , 1, with  $\text{PhC}\equiv\text{CH}$  in  $\text{C}_6\text{D}_6$  under  $\text{H}_2$  during the first 5 minutes of reaction. The resonances labelled "a" are due to the product complex 2. The peak "x" which is truncated in the later spectra is due to benzene- $\text{d}_5$ .

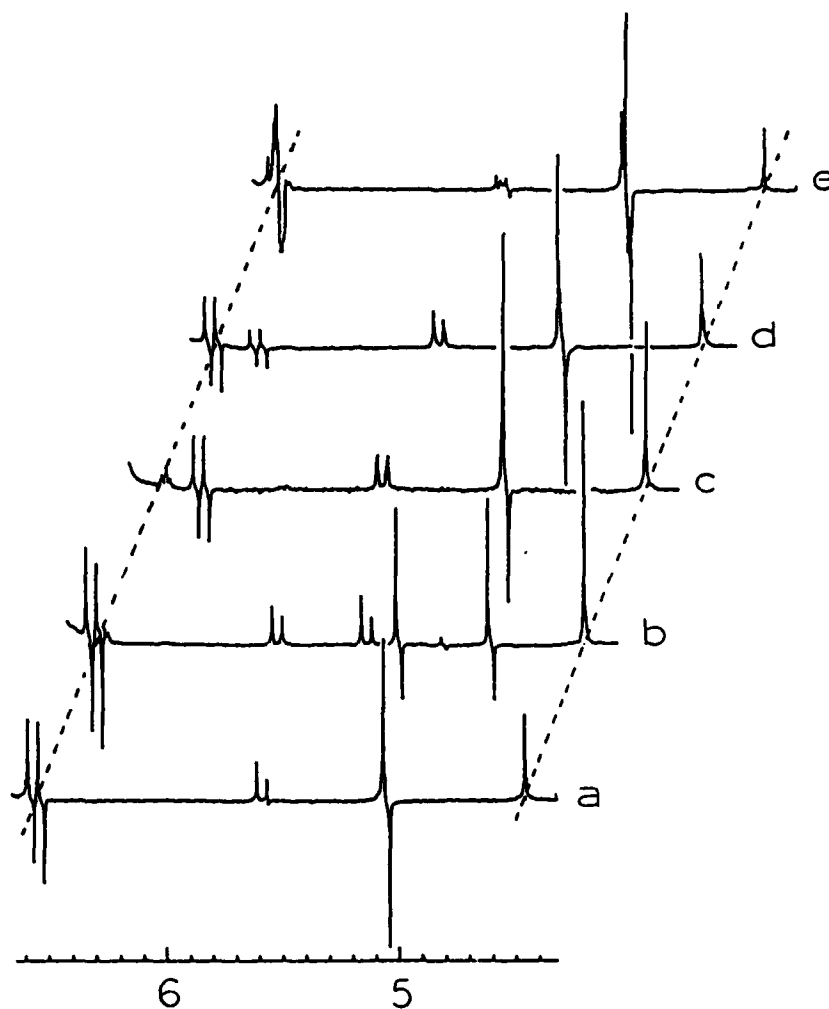


Figure 2.  $^1\text{H}$  NMR spectra at 400 MHz showing CIDNP of the styrene resonances for eqn (2) under  $\text{H}_2$ . (a) 1 +  $\text{PhC}\equiv\text{CH}$ ; (b) 1 +  $\text{PhC}\equiv^{13}\text{CH}$ ; (c) 1 +  $\text{Ph}^{13}\text{C}\equiv\text{CH}$ ; (d) 1 +  $\text{PhC}\equiv\text{CH}$  +  $\text{Ph}^{13}\text{C}\equiv\text{CH}$ ; (e) 1 +  $\text{PhC}\equiv\text{CD}$ .

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